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ERUCAMIDE-FREE CLOSURE AND LINER COMPOSITIONS

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Field of the Invention

The present invention relates to compositions for making closures and closure liners, and more particularly to compositions that are free of erucamide.

Background of the Invention

It is known to make container closures and closure sealants using polymers with erucamide as a slip agent. However, erucamides are ethylenically-unsaturated amides that react with ozone that is used for sterilization, thereby creating aldehyde off-tastes that adversely affect beverage products such as carbonated water and soft drinks. However, the use of saturated amides, such as behenamide, while avoiding the off-taste problem, tend to be less effective as slip aids because it is believed that they migrate more slowly to the surface of the matrix polymer and thereby are less efficacious in providing a low-friction surface.

As noted in World Patent WO 0236672A1 of Alphagary Corporation, it was noted that conventional closure sealants for beverage or food containers have utilized lubricants such as erucamide and oleamide, each of which is conjugated. Because these lubricants are conjugated, they are susceptible to photochemical breakdown and oxidative breakdown. In other words, oxidative breakdown of erucamide by ozone sterilization can create flavor-detracting contaminants such as ketones in addition to aldehydes. Ozone sterilization is frequently performed to sterilize bottled water products, such as mineral water and spring water. The United States Food and Drug Administration requires ozone sterilization for sterilizing bottled water products manufactured and sold in the United States. Thus, there is a need for a closure sealant lubricant that is resistant to oxidative breakdown from ozone sterilization. Additionally, there is a need for a closure sealant lubricant that is resistant to photochemical and thermal breakdown. Exposure to ultra-violet light can also photochemically degrade erucamide and form flavor-detracting chemicals, and this adverse effect can be testing using any number of industry standard tests. Degradation of erucamide can also occur as a consequence of elevated temperatures during shipping or storage in hot climates.

Thus, a novel erucamide-free composition is needed for making container closures and closure sealants.

Summary of the Invention

In surmounting the problems noted above, the present invention provides a composition, suitable for container closures and closure sealants, comprising: (A) a matrix polymer, copolymer, or blend of polymer and/or copolymers, which is essentially free of erucamide and which is essentially free of unsaturated amide; (B) a siloxane having an average molecular weight not less than 40,000 and the siloxane being present in an amount not less than 0.01parts and not greater than 10 parts based on 100 parts of the base polymer(s); and (C) a slip aid comprising a saturated amide, an oxidized polyethylene, or mixture thereof; the slip aid being in an amount not less than 0.01 parts and not greater than 8 parts based on 100 parts of the base polymers(s).

Polymers, copolymers, and blends thereof which are conventionally known for use as matrix polymers for closures and sealants are contemplated for use in the present invention.

The present invention is also directed to a lubricant/slip-aid composition for use in container closures and closure sealants. An exemplary slip aid composition comprises: a silicone lubricant (e.g., siloxane, organosiloxane) having an average molecular weight greater than 40000, the silicone being present in an amount of 0.01 parts - 10 parts based on 100 parts of matrix polymer(s) and a slip aid comprising a saturated amide, an oxidized polyethylene, or mixture thereof.

Further advantages and features are described in further detailed hereinafter.

Detailed Description of Exemplary Embodiments.

As summarized above, exemplary compositions comprise a matrix polymer; a silicone lubricant; and slip aid having a saturated amide, oxidized polyethylene, or mixture thereof.

The matrix polymer, copolymer, or blend thereof may be selected from those conventionally known for use in making containers, container closures, or closure sealants. For example, these include thermoplastic polymers such as polyethylene or ethylene copolymer with other lower alkenes, polypropylene, thermoplastic rubbers, ethylene propylene copolymers, acid modified ethylene propylene copolymers, styrene butadiene rubber, carboxylated styrene butadiene, polyisoprene, styrene isoprene styrene block copolymers, styrene butadiene styrene block copolymers, styrene ethylene butylene styrene block copolymers, polystyrene block polyethylene/propylene copolymers, polystyrene block polyethylene propylene polystyrene copolymers, polystyrene block polyethylene ethylene propylene styrene copolymers polystyrene, ethylene vinyl acetate copolymers and terpolmers, ethylene acrylate co and terpolymers ethylene vinyl alcohol copolymers, butyl rubber, ethylene acid copolymers, and polyvinyl chloride polymers.

Compositions of the invention should be essentially free of erucamide and which is essentially free of unsaturated amide. In other words, amides contained in the composition should have an iodine value no greater than 10 and more preferably no greater than 5. The iodine value is a measure of the unsaturation of alkyl groups and can be measured using the Wjis procedure, such as ASTM D2075-92, among others.

Typical examples for closure liners are described in, for instance, US 5104710, EP 0478109, EP 0599356, EP 0488491, and 0646158. The liners may be applied to the closure in any of the known methods, such as those described in, for example, US 4518336, EP 207385, and US 4277431.

Typical examples for closures are described in, for example, US 5045594, US 5186991, US 6399170, WO 0162837, EP 73334, and US 4462502.

The addition of silicones to closure and closure sealant compositions are not new, and examples of can be found in EP 129309. However, they are used in conjunction with an unsatured amide(s) to provide the ability to lessen removal torque.

In further embodiments of the invention, at least one siloxane may be used. For example, Japanese Patent Applicant No. 2000038495 described a high molecular weight siloxane as a slip aid in cap liners. However, the present inventors believe that the use of siloxanes alone are ineffective at providing sufficient ability to reduce removal torque and furthermore have the problem of polymer scuffing.

In further exemplary embodiments of the invention, a silicone can be used as a process aid. See e.g., EP 0331485. Preferred silicone lubricants are siloxanes available from Dow Corning under the trade names of DC 200® FLUID. Preferably, the viscosity of such siloxanes is greater than 50,000 cst. A particularly preferred material is also available from Dow Corning under the trade name of Si Powder Resin Modifiers and MB Master Batches, for instance, MB 50-320 and MB 50-002. The siloxanes are generally used in the range of 0.01 to 10 parts by weight based on 100 parts total polymer, the preferred range being 0.01 to 5 parts by weight based on 100 parts total polymer.

Slip aids are used to reduce the force required to remove the closure from a bottle or package. There can be found in the literature examples of the use of unsaturated amides, See e.g., JP 2002068282, US5929128, JP 02191166. However, the present inventor believes that the use of a saturated amide in a container closure or closure sealant is new. Saturated amides which are believed suitable for use in the present invention include behenamide, arachidamide, stearamide, palmitamide, myristamide, and lauramide. These are commercially available from Croda Universal. The term "saturated" as used herein shall mean and refer to compositions wherein the iodine value is no greater than 10 and more preferably no greater than 5.

Secondary saturated bis-amides are also believed to be suitable slip aids for use in the present invention. For example, ethylene bis-stearamide is commercially available as from Croda Universal under the tradename CRODA EBS. A preferred amide for use in the present invention is stearamide.

Oxidized polyethylenes, with or without the saturated amide, are also believed to be suitable slip aids for use in the present invention. These are commercially available from Honeywell under the tradename A-C, one particularly preferred version being named or otherwise denominated "A-C 629A." The typical ranges of both these types of slip aides are 0.01 to 8 parts based on 100 parts of the base polymer(s).

Optional components for use in the compositions and methods of the invention include pigments, antioxidants, stabilizers, UV stabilizers, UV absorbers, molecular sieves, hydrocarbon oils, phthalate ester plasticizers, epoxidized soyean oil, foaming agents, acrylic processing aides, fillers, and nanocomposites. Additionally active packaging components may be included such as oxygen scavengers, aldehyde scavengers, anti-microbials, and flavor enhancing agents.

Exemplary compositions of the invention may be formed, such as by molding, into beverage or food containers, closures, or closure sealants such as cap linings.

The present invention also provides slip aid compositions. An exemplary slip aid composition for use in container closures and closure sealants, comprises: a silicone (e.g., a siloxane, an organosiloxane such as poly(dimethyl)siloxane having an average molecular weight not less than 40,000, said silicone being present in an amount not less than 0.01 parts and not greater than 10 parts based on 100 parts of said base polymer(s); and a slip aid comprising a saturated amide, an oxidized polyethylene, or mixture thereof; said slip aid being in an amount not less than 0.01 parts and not greater than 8 parts based on 100 parts of said base polymer(s).

The foregoing embodiments and examples are provided for purposes of illustration only and are not intended to limit the scope of the invention. In the examples, the following abbreviations are used:

EVA-1	Ethlyene-vinyl acetate copolymer, 14% VA
EVA-2	Ethylene-vinyl acetate copolymer, 9% VA
EP	Ehtylene-propylene copolymer
ER	Crodamide™ ER
SR	Crodamide™ SR
EBS	Crodamide™ EBS
Si1	Dow Corning™ 200 fluid, 60000cst
Si2	Dow Corning™ 200 fluid, 100000cst
Si3	Dow Corning™ MB50-320
Si4	Dow Corning™ MB50-002
AO	antioxidant
BLUE	pigment
OXP	Oxidized Polyethylene
UV1	Tinuvin™ 622
UV2	Uvinul™ 3030

Example 1

The compositions in table 1 below were blended, extruded into films, and 1 inch discs punched out. The discs are then inserted into 28 mm polypropylene caps

designed for carbonated soft drink applications. The caps are then applied to 20 oz. PET bottles filled with water using a commercial application machine. The bottles are stored at room temperature for less than week and greater than 24 hours, after which, the force required to remove the cap was measured and any tearing, scuffing or stringing of the liner is noted.

Table 1

	A	B	C	D	E	F	G
EVA-1	90	90	90	90	90	90	90
EP	10	10	10	10	10	10	10
AO	0.1	0.1	0.1	0.1	0.1	0.1	.1
BLUE	0.8	0.8	0.8	0.8	0.8	0.8	.8
ER	0	1	0	0	0	0	0
EBS	0	0	1.5	0	0	0	0
SR	0	0	0	1.5	0	0	0
OXP	0	0	0	0	1	0	0
Si1	0	0	0	0	0	1	0
Si2	0	0	0	0	0	0	0
Si3	0	0	0	0	0	0	2
Removal Torque, in-lbs.	>23.6	10.6	>24.2	20	20.6	16.7	13.2
Stringing/ Scuffing	100%	10%	70%	80%	40%	100%	100%

As shown above, no one lubricant or slip aid alone provided the same degree of performance as erucamide. Stringing and/or scuffing of the liner was believed to be caused from the bottle surface tearing the liner. In the food and beverage industry, this is considered unacceptable as it can cause pack contamination. An insufficient lubrication/slip property on the surface of the liner will cause this to worsen.

Example 2

In accordance with the procedure described above for Example 1, the following compositions were applied to caps and tested, as shown in Table 2 below.

Table 2

	A	B	C
EVA-1	90	90	90
EP	10	10	10
AO	.1	.1	.1
BLUE	.8	.8	.8
Si3	3	3	0
Si2	0	0	1.5
SR	0	1	1
OXP	1.5	0	.5
REMOVAL TORQUE, IN-LB.	13.6	10.3	12.0
STRINGING/ SCUFFING	0 %	0 %	14 %

This data indicates that by utilizing a mixture of siloxanes and ethylenically unsaturated amides and/or oxidized polyethylene, in combination, provided performance equal to that of erucamide.

Example 3

In another example, the compositions identified in table 3 are extrusion blended and pelletized. The pellets are melted in another extruder and applied to caps using a well-known method *(See e.g.*, European Patent No. 207385).

The resulting lined caps are allowed to age at room temperature for a minimum of 1 week before being subjected to testing (of removal torque required to remove caps from PET bottles). The caps are applied to 500 ml PET bottles filled with carbonated water using a commercial application machine. The capped bottles are stored at both cold and room temperature, and removal torque measured is after given storage periods. Results are presented in Table 3 below, with Column A representing erucamide-free liner formulation and Column B representing erucamide-containing formulation, with units presented as parts per hundreds of resin (PHR).

Table 3

Liner Formulation	A	B
EVA-2	100	100
AO	0.1	0.1
BLUE	0.8	0.8
ERUCAMIDE	0	1.0
Si 4	0.8	0
Si 2	1.3	0
SR	0.3	0
OXP	0.8	0
Removal Torque, in-lbs.		
24 Hrs. @ 4°C	13.8	15.3
1 week @ 4°C	14.3	16.2
1 week @ 23°C	11.1	11.0

This data indicates that the use of mixture of siloxanes, ethylenically unsaturated amides and oxidized polyethylene, in combination does provide torque removal performance equal to or better than that of erucamide-containing cap liner formulations.

Example 4

In another example, compositions similar to above are extrusion blended and pelletized. The pellets are then melted in another extruder, and the molten pellets were transferred directly from the extruder to the individual cap and immediately compression-molded.

The resulting lined caps are allowed to age at room temperature for a minimum of 1 week prior to testing. The caps were then applied to 20 oz. PET bottles filled with water using a commercial application machine. The bottles were stored at 40°F for less than week and more than 24 hours. After this period, tests were performed to measure the force required to remove the cap, and any tearing, scuffing or stringing of the liner was noted.

Compositions containing a siloxane in conjunction with an ethylenically unsaturated amide and/or an oxidized polyethylene slip aid gave removal torques comparable to compositions containing erucamide. Stringing was judge to be

commercially acceptable by industry standards. However, a composition using a siloxane alone without an unsaturated amide and/or oxidized polyethylene gave unacceptably high removal torque and stringing.

Example 5

In another example, compositions in table 4 are extrusion blended and pelletized. The pellets were re-extruded into tape form about 17 mils thick. One inch diameter disks are punched out from the tape and placed in clean glass jars. The jars are stored at 115°F for four days, removed and held at 68°F for one day. Three disks are removed from the glass jars, and two are inserted into twenty ounce PET bottles plus one disk inserted into a commercial 28mm cap. The bottles are filled with distilled water, capped, and placed at 115°F storage for 6 days, then stored at 68°F. The water samples are given to a trained sensory panel and evaluated using the flavor profile method, which is a recognized industry standard. The erucamide free formulation had consistently lower flavor and odor intensities than the erucamide control.

Table 4

	A	B
EVA-1	90	90
EP	10	10
AO	.1	.1
BLUE	.8	.8
ERUCAMIDE	0	1
Si3	.8	0
Si2	1.3	0
SR	.3	0
OXP	.8	0

Example 6

In yet another sensory example, composition in table 5 is extrusion blended, pelletized, and re-extruded into tape. A sample of the current commercially used liner compound for mineral water is extruded into tape and used as a control. Disks are punched out of the tapes and inserted into transparent commercial 28-mm plastic caps. Clear glass bottles with a 265 ml volume are filled with water, headspaced at

5% volume, and hand closed. The bottles are placed in a suntester under the following conditions:

Xenon bulb Nxe-1500A

Quartz filter: 290nm

Distance from filter to cap: 17 cm.

Exposure time: 42 hours.

A trained panel using the triangular test method is then evaluated the water samples.

Table 5

	A
Si4	.8
Si2	1.3
SR	0.3
OXP	0.8
EVA-1	100
AO	0.1
BLUE	0.8
UV1	0.3
UV2	0.25
Sensory Results as compared to commercial control	
Significance	96%
Difference	6
Preference	A
Difference scale of 1-13, 1 is very slight, 13 is very strong	

Sensory results after exposure to ultra-violet light show the erucamide free compound to be significantly preferred over the commercial control.

By utilizing a mixture of siloxanes and ethylenically unsaturated amides and/or oxidized polyethylene, in combination, torque removal performance equal to that of erucamide was obtained by compositions of the present invention.

The foregoing embodiments and examples were provided for illustrative purposes only and not intended to limit the scope of the invention.